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Materials for Fuel Cells

L. H. Bennett, M. I. Cohen, A. L. Dragoo, A. D. Franklin and A. J. McAlister

Institute for Materials Research
National Bureau of Standards
Washington, D. C. 20234

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ABSTRACT

This report describes the research plans and initial progress on the NBS program of research on Materials for Fuel Cells.

Transition metal carbides, borides, and nitrides ("refractory hard metals", or RHM) are being examined as potential hydrogen oxidation electrocatalysts for use in acid fuel cells. Preliminary screening of 19 carbides and borides has revealed apparent stability in hot (up to 160°C) phosphoric acid for TaB, MoB, NbC, TaC, Mo₂C, and WC. More sophisticated tests for acid stability for these materials are under way. Equipment for examination of the electrochemical behavior of these materials as hydrogen oxidation electrocatalysts in phosphoric acid electrolytes at temperatures up to 150°C is being completed, and tests will be started on these materials shortly. Additional materials in the general RHM class, including a number of nitrides, have been ordered and will be screened for acid stability. More extensive exploration will be made of the properties of TaC and WC as a function of stoichiometry and presence of other metals and of oxygen.

Plans exist for a parallel study of oxides as oxygen reduction electrocatalysts for acid fuel cells, supported by NBS. The current effort is devoted to improving and expanding the facility for electrochemical measurements.

The long-term stability of CeO₂-based solid electrolytes, which are promising new candidate materials for the high-temperature fuel cells, is under study. Materials for fabricating specimens of CeO₂ doped with Gd₂O₃ or Y₂O₃ have been obtained or ordered, and arrangements made to hot press them. Experiments have been designed to examine degradation of the electrical properties at temperatures from 500°C to 1100°C, with and without a constant

current throughout the degradation anneals. Compositions will be chosen around those giving a maximum conductivity, and the oxygen partial pressure will be fixed at a convenient value. AC admittance measurements will be used to monitor the electrical properties. Furnaces and ancillary equipment are being assembled or constructed.

1. Introduction

The National Bureau of Standards is undertaking a program of research on materials for fuel cells, with an especial, long-range, emphasis on problems relating to lifetime and the assessment or testing of expected life of particularly the electrically active components of fuel cells. Such components include, for instance, the electrocatalysts in liquid-electrolyte cells, and the solid electrolyte in high-temperature cells. This report will describe the entire program in order to provide the context for the subject project, but will report detailed progress on the latter only.

The Materials for Fuel Cells Program at NBS consists of three major elements, which taken together reinforce each other in techniques and concepts, but each of which may also stand alone. These embrace:

- i. Electrocatalysis, especially oxygen reduction, on non-metallic surfaces;
- ii. Electrocatalysis, especially hydrogen oxidation, on non-noble metals and alloys; and
- iii. Degradation mechanisms involving solid oxygen-transporting electrolytes.

The subject project contains work on items ii and iii.

2. Technological Motivation

Fuel cells offer considerable potential benefit in terms of conservation of fuel and minimum environmental impact for the generation of electricity from fossil fuels.

The major potential immediate uses for fuel cells include the delivery of peak power in central station operation, the distributed generation of electricity on the neighborhood or local level [1], and replacement of

small generators for rural and small municipal power plants and in urban locations [2]. These potentialities draw upon the considerably higher efficiency of even present fuel cells systems, as compared to conventional generators, when operating under partial load, and their low environmental impact. In addition, as liquid primary fuels become scarce, fuel cells, like batteries, may have potential for vehicular use.

The major present thrust in the electric utility field [3,4] is the hot ($\sim 150\text{-}180^{\circ}\text{C}$) concentrated phosphoric acid fuel cell. This cell uses hydrogen and air, and with a reformer can burn hydrocarbon gases. It has the great advantage of lack of sensitivity to CO_2 in the fuel or the air. Alkaline fuel cells have also been highly developed, but, because of their sensitivity to CO_2 , only for special applications such as the Apollo program.

The major limiting problems [5] in these cells are concerned in the first instance with cost, and therefore also lifetime, and secondly, with efficiency. In the acid cell the only electrocatalyst so far capable of achieving the needed performance is platinum. With Pt electrocatalysts of particle size large enough to be stable over the desired lifetime (5 years, or 4×10^4 hours) the loading is so high that the cost is prohibitive. If the particle size is made sufficiently small so that the cost is reduced enough to make first-generation (1975-80) cells commercially attractive, the lifetime cannot be achieved because of sintering of the Pt particles. Ultimately, also, the Pt will probably have to be replaced altogether to meet the cost requirements of the more general use contemplated beyond 1980. Other metals or alloys, and metal oxides or other compounds are possibilities.

Furthermore, at the air electrode in both acid and alkaline media, present catalysts (including Pt) reduce the oxygen to peroxide rather than to water. The working voltage for the peroxide reaction is lower than that

possible with the water reaction, and therefore the achievable efficiency of conversion of chemical to electrical energy is also lowered. The development of catalysts for oxygen reduction, particularly in the acid cell, that avoid the peroxide reaction or minimize it could result in significant increases in efficiency that may be necessary in the second-generation cells and beyond.

Besides the low-temperature acid cell, another fuel cell with rather large potential for fuel saving is the high-temperature solid-electrolyte cell, directly coupled into hot product gases of a coal combustor. This combination on paper should produce efficiencies better than 60% in the conversion of fuel chemical energy to electrical energy.

The materials problems at the high operating temperatures ($\sim 1000^{\circ}\text{C}$) are severe, however. In particular, the electrical connection between cells must be a good electronic conductor at this temperature over a range of equivalent oxygen pressure from that of air to that of the fuel. At the same time it and all other components must also, in the interest of economic operation, be not too costly and be stable over the design lifetime. These problems have proved so severe that serious development in this country ceased for a period and only recently has been renewed.

Reduction in operating temperature would help considerably in meeting these problems. In the past, this temperature was dictated by the temperature dependence of the conductivity of solid electrolyte (stabilized ZrO_2) and the practical lower limit to the thickness of films formed under production conditions. Recent work [6,7] on CeO_2 -based materials has demonstrated the possibility of oxygen-conducting solid electrolytes capable of operating at significant lower temperatures. However, these indications are quite preliminary and little is known of the stability of such materials under

current-carrying conditions. Furthermore, although electrode polarization is not a serious problem at the higher temperatures, some is evident at both electrodes. It must be expected to become more serious as the temperature is reduced, with a resultant loss in efficiency.

From the above discussion, it is evident that some of the most important problems standing in the way of realizing practical fuel cells involve the electrodes and the catalytic and other processes that occur there. On the other hand, successful development of fuel cells for power generation could provide real savings in the use of fuel.

3. Program and Progress

3.1 Non-Noble-Metal Electrocatalysts

3.1.1 Electrocatalysis on Non-Noble Metals and Alloys

Objectives

To use the results of combined studies of electrochemistry and solid state properties (particularly the relationship between the electronic properties such as the density-of-states in the d-bands and electrocatalytic activity) of the refractory hard metals to identify materials with promise for efficient electrocatalysts. Emphasis is on hydrogen or fuel oxidation and the replacement of Pt for this purpose in acid fuel cells.

Scientific Motivation

Correlations have been noted between the electrocatalytic efficiencies of Group VIII metals and rough features of the electronic density of states. For example, the O_2 reduction rate in orthophosphoric acid of a number of pure precious metals and their alloys among themselves has been shown [8] to be maximal at a d-band vacancy level of ~ 0.6 . Correlations of this sort are of limited use, in that the parameters are neither well defined nor sufficient to describe the complex electronic structure of the materials studied. Other

features may be important to electrocatalytic activity, such as the magnitude of the density of states at the Fermi level $N(E_F)$, or the occurrence of exchange enhancement. In fact, the importance of $N(E_F)$ has been stressed by Levich [9].

Refractory hard metals -- compounds of transition metals with the metalloids B, C, and N and hereafter referred to as RHM -- have transition-metal-like physical properties. They are electrical conductors, often with higher conductivity than the transition metal hosts; and generally have higher melting points and greater chemical stability than the host transition metal. While little is yet known of the detailed electronic structure of these materials (partly due to difficulties in preparing pure, single phase samples), the available data do indicate that in these compounds, transition metal site d-densities of states resemble those of pure metals of higher group number. For example, we have observed such d-band behavior in studies of the state densities of first transition series metal diborides [10] and of the carbides WC and Mo_2C [11].

Thus, the RHM have electronic structures similar to that of Pt in the essential feature of incomplete d-bands, and may well be catalytically active for hydrogen oxidation (at least two are known to be: WC [12], Ni_2B [13]) and may well be acid resistant as well (at least one is known to be: WC [12]). Available data on the hydrogen oxidation activity and acid resistance of the RHM are far from exhaustive, and in some instances questionable, largely from the standpoint of sample quality. To date, only WC of the RHM is in active use, [14], and even here it is not yet clear what the exact composition of the active form is; there is some evidence to suggest that pure WC is catalytically inactive [15], and that the active species (activity being a very sensitive function of preparation method [16]) is perhaps tungsten rich

[15] or has at least a partial substitution of oxygen at carbon sites [17].

Research Program

The work will consist of a direct evaluation, using well-characterized specimens of RHM which, by virtue of their electronic structures, promise to be catalytically active. A parallel effort is planned, currently under NBS sponsorship, to continue to study oxides as oxygen reduction catalysts and to initiate studies of the activity of WC, alloyed at both metal and metalloid sites, with a view to determining the precise nature of the active species and the effect of alloying, and to conduct studies of the acid resistance and activity of the alloy system TaC_x , $0.8 < x < 1.0$ (which displays [18] a wide variation in conductivity and other physical properties with x) to determine the effects of stoichiometry.

Our immediate aim is the study of the compounds Mo_2O and Cr_3C_2 for which we expect catalytic activity and anticipate good acid stability. We shall conduct a screening program for acid stability of various, well characterized RHM as they become available to us. Presently, these include Mo_2C and Cr_3C_2 as mentioned, as well as the diborides of Sc, Ti, V, Cr, Zr, Hf, and Ta; the monoborides of V, Cr, Ta, Nb, and Mo; and the monocarbides of V, Nb, and Ta. Other materials, including nitrides, phosphides, and silicides, will be screened as acquired. Validity of literature data will be tested, particularly where doubt of a sample quality exists.

Alloyed WC, particularly with oxygen substituted at the metalloid site, and various TaC_x samples will be prepared at NBS, characterized, and tested as available.

In background studies, not part of the subject project but to be carried on as part of the larger program, it is proposed to focus attention on rather

complete investigations of the transition metal diborides, and to initiate studies of the cubic monocarbides. Theoretical interpretation by band theoretical techniques will stress systematic variation in d-band densities through these isostructural sequences of compounds; similarities between their electronic structures and those of the Group VIII metals; and correlations of their densities of states and electrode performance as measured by relatively standard electrochemical test methods. The results of electrochemical testing will be used as feedback for suggesting which electrode properties and structures should be looked for.

Sample preparation and characterization must be emphasized in such an investigation. Our own experience indicates that preparation of pure, single phase materials is difficult, and leads us to question much of the available data on the physical and chemical properties of these materials. As a specific example, consider high temperature oxidation data on transition metal diborides. All samples of these materials that we were able to obtain for our studies contained significant amounts of BN and BC; it is therefore questionable as to whether high temperature oxidation data on these materials reflect properties of the diborides or of the occluded contaminants. Similar uncertainties must be avoided in the present investigation.

Experimental tools for study of the electronic density of states include x-ray photoemission, which probes the local transition metal d-state density, both bulk and surface via variation of x-ray incidence and electron takeoff angles; soft x-ray emission which probes the local p-like state density at metalloid sites and yields information on the d-like structure through metalloid s- and metal d-hybridization; and nuclear magnetic resonance. Mossbauer effect and perturbed angular correlation studies will be used where appropriate; the latter, owing to its great sensitivity to local variations

in electric field gradient is an appropriate tool for study of sintering of electrode particles. Magnetic susceptibility, x-ray diffraction, and metallography will also be employed.

Progress to Date

Our work in this area involves 1) preparation and characterization of materials, 2) screening of these materials for stability in hot phosphoric acid and 2) examination of stable materials for electrocatalytic activity through potentiodynamic current-voltage measurements. The first two of these efforts are well underway, and we shall describe our results to date. For the second phase, equipment is very nearly complete, as described elsewhere in this report, and work will begin very soon on candidate materials (5 to date) suggested by the screening program. Some problems and progress on sample and electrode fabrication will be discussed here as well.

Our screening procedure for acid stability consists of a) visual inspection for signs of instability (bubbling, change of color of solution, or changes in color or state of candidate material) in 85% H_3PO_4 at room or elevated temperature, and b) comparison of initial sample mass with insoluble residual mass after long exposure to 85% phosphoric acid at 80°C.

To date, some 19 materials have been examined, with five showing promising stability. All are listed in Table 1, the promising materials being starred. Long term weight loss studies are now being conducted on the latter.

Table 1Stability of Refractory Hard Metals in H_3PO_4

Cr_3C_7	fc	CrB	fh
Cr_7C_3	fh	VB	fc
		NbB	fc
FeB	fc	TaB (good)	p*
Fe_2B	fh	TaB (bad)	fh
		MoB	p*
Ni_3P	fh		
Ni_3MgB_2	fc	TiC	lp
		zrC	lp
TiB_2	fh, lw	VC	lp
ZrB_2	lw	NbC	p*
HfB_2	lw	TaC	p*
VB_2	lw	Mo_2C	p, lp*
NB_2	lw	WC	p, lp*
TaB_2	p, lp	W_2C	fc
CrB_2	fc, lw		

Key:Present work: in 85% H_3PO_4 fc failed, visible reaction in cold (22°C) H_3PO_4 fh failed, visible reaction in hot (80 or 160°C) H_3PO_4 p no visible reaction, to be given long term weight loss test in 80°C H_3PO_4

* long term wt. loss tests underway.

Literature

lw excessive weight loss reported in literature, drop.

lp small weight loss reported in literature, consider further.

Other materials for study are now being obtained or fabricated. In Table 2 are listed materials ordered for screening tests. (Many of these purchased materials will be of less than ideal quality, but should be adequate for the screening tests).

Table 2

List of Ordered Materials

Cr_{23}C_6	Cr_2N	WB
HfC	HfN	W_2B
NbC	NbN	W_2B_5
Nb_2C	TaN	
TaC	NiN	
Ta_2C	ZrN	
TiC		

Work is underway to produce samples of known surface area by gaseous carburization, boriding, or nitriding of metal sheet. High quality sheet samples of WC and TaC have been produced in this way. We are attempting now to vary stoichiometry in TaC so produced, principally by control of gas pressure. Scheduled for early trial are attempts at alloying WC with other metals at W sites and with oxygen at carbon sites. We suspect that the latter effect is achieved by pretreatments and preparation methods currently used to produce active WC for fuel cell electrodes. Oxygen substitution for carbon is our interpretation of the recent experiments of Ross and Stonehart, who found that of a variety of WC samples obtained from different sources, only that specially prepared by AG-Telefunken was active in hydrogen adsorption.

The problem of preparing test electrodes of known geometrical area is being pursued in two ways. One, the preparation of sheet samples has already been mentioned. We have tried a variety of binding materials for use with powder samples, with the aim of producing a conducting, non-porous electrode whose active geometric area can be estimated by metallographic techniques. The most stable binder in hot phosphoric acid, teflon, generally yields porous electrodes. Electrochemical area determinations will also be carried out where possible.

3.1.2 Electrocatalysis on Non-Metallic Surfaces

This part of the overall program is not **under the subject contract**, but will be discussed here to present as complete a picture as possible of the entire program.

Objectives

1. To elucidate the mechanisms of oxygen reduction on non-metallic electrocatalytic surfaces.
2. To find efficient non-metallic electrocatalysts as replacements for Pt, preferably capable of electroreducing oxygen directly to hydroxyl rather than through peroxide, and of functioning in hot concentrated acid electrolytes.

Scientific Motivation

Semiconductors have long been used as heterogeneous catalysts, especially for oxidation and reduction reactions. Early materials used as electrocatalysts [19] included the oxides of Cu and Ga. Silver has found extensive use at the oxygen electrode in alkaline fuel cells [20], and may well operate as an oxide. Lithiated NiO at temperatures above about 100°C has also operated successfully as an oxygen electrode in alkaline media [21]. More recently, work has been done using spinels [21] such as CoAl_2O_4 and perovskites such as Sr-doped LaCoO_3 [22]. The latter use is obviously related to the use of the

perovskites ABO_3 , where A represents rare earth, Pb, or alkaline earth ions, and B is Co or Mn, for oxidation of CO and reduction of NO_x in automotive exhaust catalysts [23]. Some of the early, exciting non-metallic electrocatalysts, for both hydrogen oxidation and oxygen reduction, were the tungsten bronzes and related compounds [24, 25, 26]. However, more recent work has shown that the observed high catalytic activity depends upon the presence of Pt [27, 28], which in some way activates the oxide in a synergistic fashion.

A fairly detailed body of theory has been worked out for electrochemical processes on semiconductors and insulators [29], but most of the application has been to very well-characterized semiconductors such as Ge, Si, GaAs, ZnO, and CdS. Recently Tench and Yeager [30] have applied these ideas to a study of lithiated NiO. The present proposal is to carry this sort of work forward to the study of materials more closely related to those that may play a role in acid electrolytes as oxygen catalysts.

Previous work in these laboratories [31] has uncovered a number of candidate materials exhibiting stability in concentrated phosphoric acid at 100°C . These include oxides of Ta and Nb with various transition metals, and also $BaRuO_3$. The latter also showed some promise as a catalyst for oxygen reduction, although under strong oxidizing conditions in the hot acid a deterioration of the electrochemical activity occurred. A new class of compounds based on $CeTaO_4$ also appears interesting in that considerable conductivity can be built in by adjusting the oxygen content and also presumably by doping, and yet acid stability is to be expected. The materials to be studied will be chosen from among such materials, with perhaps also IrO_2 or RuO_2 , which although not acid stable do give some evidence of catalyzing oxygen reduction without going through peroxide [32].

Research Program

Because the mechanisms of reduction reactions on non-metallic electrode materials are not well enough understood to serve as much of a guide in the selection of electrocatalytic materials, it is proposed to combine a study of electroreduction mechanisms on non-metallic electrodes with a continued search for promising non-metallic electrocatalysts, especially for oxygen reduction in acid media.

1. Mechanism of electroreduction

Oxygen reduction is a complex process that may involve a number of simultaneous reactions [33]. As a probe for at least the initial phases of a study of electrocatalytic mechanisms, oxygen reduction may present too difficult a problem in interpretation. For this reason it is proposed to use also one or more simpler redox reactions, of which a number are available. For instance, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ couples exhibit simple mechanisms from the viewpoint of reaction kinetics [34]. On the other hand, the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ couple, although not as well studied, is relatively stable over a wide pH range and would allow examination of the influence of hydrogen ion concentration on the electrode kinetics [35].

The initial experiments, conducted in supporting electrolyte only, without the redox system present, will be designed to elucidate the potential distribution within the combined electrode-electrolyte system (space charge, double layer, etc.) and the changes taking place in the electrode surface (adsorbed species, valence changes, etc.) as a function of potential [29]. Conventional voltammetry will be combined with ac impedance measurements,

ellipsometry, and perhaps electroreflectance to yield this information [30]. Electrolytes of various pH's will be used, and the influence of temperature and adsorbable ions studied. Changes in the chemical composition of the electrolyte will be monitored.

The electrochemical measurements in the presence of the redox couple will be performed with a rotating electrode to allow study of the mass transport aspects of the faradaic currents. The study will involve the dependence of the current on potential, rotation, pH, and other compositional variables to determine the mechanisms of reduction and the exchange current (reaction rate) as a function of pH and other measures of the electrolyte composition. The impedance measurements in the initial experiments should allow correction to the applied potential across the cell for that portion across the electrode itself and therefore not effective in the electrical reactions.

To interpret the electrochemical phenomena we will need to know more about the electronic properties of the electrode material [36]. If possible, single crystals will be grown for this part of the study. Measurements as a function of temperature, atmosphere, and doping will be made of such electronic quantities as conductivity, Hall effect, and thermopower. For the most part the materials of interest appear to contain transition metal ions and magnetic susceptibility and perhaps EPR may be very valuable in sorting out the nature of the important electronic states. These data will be used to explore the electronic structure (including the band or localized nature of the d-levels, the density of states, etc.), to identify the charge carriers and conduction mechanisms, to determine the energy levels of donor or acceptor states and of the Fermi energy, and to obtain data on the numbers and mobilities of charge carriers.

Finally, because the electrocatalytic reactions of interest take place on the interface between the electrode and the electrolyte, details of the chemistry and structure of that interface will also be studied. The macroscopic topographic features of the initial surfaces can be explored by a variety of available microscopic techniques, and the initial chemistry by x-ray emission analysis, etc. Something of the nature of the adsorption chemistry can be learned by studies of the relatively simple species adsorbed from the gas phase, using optical spectroscopy together with measurements of the adsorption isotherms. With the expected transition metal ions present, there may be a real opportunity to learn of the electronic interactions of adsorbate groups with the surface using sensitive magnetic susceptibility measurements or EPR. Also needed will be in-situ studies of the behavior of the surface exposed to the electrolyte and under varying potential. Optical methods (e. g., electroreflectance, ellipsometry, reflectivity) should be particularly suited to exploring the surface electronic states of the electrode material, the development of surface layers, and the nature of adsorbed species.

The results of these efforts should be a picture of the electronic structure of the electrode material and its behavior under electrochemical conditions. The way this structure and behavior influences the kinetics of the redox reactions studied should then be better understood [29], and clues should be obtained as to how to modify the material to optimize its performance as a redox catalyst. At this point in the program it should then be profitable to turn to a systematic examination of oxygen reduction as the electrochemical process.

2. Search for acid-resistant potential oxygen-reduction electrocatalysts.

Research will be directed toward the preparation and characterization of new, acid stable, oxide materials which also are reasonable electronic conductors. Previous work [31] has demonstrated that mixed oxides containing Ta_2O_5 and/or Nb_2O_5 exhibit remarkable stability in concentrated phosphoric acid at $100^{\circ}C$. For this reason, research efforts will continue to focus on oxide systems containing these components. Furthermore, systems which afford reasonable potential for development of conducting materials will be selected for study. Electronic conductivity in crystalline oxides often results from gross nonstoichiometry compensated by cations which exist in multiple oxidation states. Candidate systems, therefore, also will include oxide components such as those of the transition metals and some of the rare earths. Additionally, attempts will be made to enhance the conductivity of new oxide materials by doping with suitable components.

Although the primary objective of these studies will be to develop new oxide materials for electrocatalysis, it is anticipated that important correlations will be made among phase nonstoichiometry, electrical and magnetic properties, and catalytic activity. These correlations will serve as input to determine the direction of continued exploratory work.

Experiments will be done, using such techniques as x-ray diffraction, thermogravimetry, DTA, etc., to outline the phase relations of the candidate systems, including oxygen partial pressure as a variable. Promising phases will then be screened for acid stability by following the loss in weight of pressed specimens rotated in concentrated phosphoric acid at 100° to $150^{\circ}C$. Changes in near-surface chemistry as a result of this treatment will be examined using x-ray diffraction. The influence of compositional changes within promising phases on the electronic properties will be followed using measurements of conductivity, magnetic susceptibility, etc.

Progress To Date

Previous work on this part of the program is reported [31] under Contract EPA-IAG-D4-0528. Since then the work has been solely on upgrading the facility for electrochemical measurements on electrocatalytic materials.

The central measurement facility is a potentiostatically - driven cell capable of operating both as in the potentiodynamic scan mode, primarily with linear sweep but also with a variety of waveforms, and also in a galvanostatic mode for steady-state voltammetric measurements. Studies using cyclic voltammetry, steady-state current-voltage measurements, and adsorption at the electrodes will be possible.

This apparatus has been modified to allow operation at temperatures up to 150°C while controlling the nature and flow of gas (N_2 , O_2 , H_2) to the cell. An optical window allows illumination of the experimental electrode. The output is recorded either with an x-y recorder, or for very rapid scans with a storage oscilloscope.

It is planned in the future to add rotating disk and ring electrodes to study formation of intermediates during the electrode reactions. Such information will be of greater value for the study of materials as electrocatalysts for oxygen reduction than for hydrogen oxidation. It can also be very useful for studies of the chemical stability of the electrode itself.

Finally, it is planned to add modern equipment for determining the complex impedance of the electrodes over a wide range of frequencies, temperatures, bias potentials, and electrolyte compositions. In order to pursue these and other measurements most efficiently, an automated system based on microprocessor control has been designed and is being constructed.

3.2 High Temperature Solid Electrolytes

Objectives

1. To determine the long-term stability of oxygen-transporting solid electrolyte-electrode systems at high temperatures and to elucidate the mechanism producing whatever degradation occurs in bulk transport properties and in electrode-electrolyte interfaces.
2. To develop reliable lifetime tests for these systems as needed.

Scientific Motivation

Developmental work on high temperature fuel cells using solid electrolytes has been concentrated almost wholly on the use of ZrO_2 stabilized with CaO (about 15 mole %) or Y_2O_3 (about 10 mole %). Work has been done [37] principally at Westinghouse and G. E. in the United States, and elsewhere in France, Germany, and Russia. In the United States, only Westinghouse has carried on development work in the recent past.

The Westinghouse cell [38] consists of a thin membrane of stabilized ZrO_2 electrolyte, which conducts electricity almost completely by oxygen ion transport, with an air electrode of a metal oxide (e. g., In_2O_3 doped with Sn, Sb, or Te) and a Ni fuel electrode. At the temperature of operation, 1000°C , both H_2 and CO are oxidized. Attainable voltage efficiencies are estimated as better than 70 percent. The limiting electrochemical factors in attaining the design characteristics appear to be the electrolyte resistivity, the interconnection resistance, and the fuel electrode polarization voltage drop. Lifetime appears to be the major unattained design requirement, and, of course, is closely tied to cost and economic feasibility. The Westinghouse Final Report [38] quotes a target lifetime in service of five years. Life tests were described in which cells operated for 50 days or more at temperature with no apparent deterioration in performance. However, the interconnection between cells was not stable.

A reduction in operating temperature would undoubtedly bring great improvement in lifetime of materials and components. The ZrO_2 electrolyte requires an operating temperature of 1000°C to attain the necessary conductivity, about $10 \, \Omega^{-1} \text{ m}^{-1}$. Recent results [6,7] on $\text{CeO}_2:\text{Ln}_2\text{O}_3$, where Ln represents a variety of lanthanide ions, have revealed that essentially equivalent oxygen conduction occurs at substantially lower temperatures. The door being open to lower-temperature operation, there is hope that some of the stability problems can be overcome. However, the long-term stability of the candidate electrolyte materials and of the electrolyte-electrode interfaces should be investigated.

Indeed, solid electrolytes of this kind, containing deliberately-added impurity ions, must be expected under continual exposure to the high temperatures ($700^\circ - 1000^\circ\text{C}$) and constant electrical potential differences (about 0.8 volts across approximately 20 microns, or fields of the order of 400 volts/cm) to undergo several slow changes that should lead to degradation of desirable fuel-cell characteristics and substantial loss of efficiency. These include:

1. Ordering of Dopant Ions (Ca^{2+} , Y^{3+} , Ln^{3+} , etc.)

This effect is known to occur in most (but not all) stabilized zirconia specimens with compositions near that exhibiting maximum conductivity [39,40]. For instance, for annealing times of several thousand hours at 1000°C (the proposed Westinghouse Fuel Cell operating temperature), polycrystalline samples of calcia-stabilized zirconia develop x-ray and neutron diffraction patterns corresponding to the ordered arrangement of Ca^{2+} ions on the cation sites. At the same time the resistivity increases strongly. The effect occurs much more rapidly in single crystals than in

polycrystalline specimens. In the latter, the rate varies from specimen to specimen, and in some, was not observed after three months annealing. Similar effects probably occur in the ceria-based materials as well [6]. It seems likely that judiciously chosen impurities can probably inhibit the effect. For attainment of a consistent five-year life, however, further examination of the effect to insure that lifetime seems required. While similar studies of CeO_2 -based electrolytes don't seem to have been made as yet, it seems likely that ordering of impurity cations can also occur in that system.

2. Migration of Dopant and Impurity Ions

The desirable high-conductivity cubic phase of ZrO_2 occurs only with at least about 7-10 mole percent of added oxides such as CaO or $\text{YO}_{1.5}$ ($1/2 \text{ Y}_2\text{O}_3$), and the conductivity exhibits a fairly sharp maximum as the composition changes across the cubic phase. Similar maxima occur with doped CeO_2 [41] compositions. Under the electric fields that will be imposed on the fuel cells in continuous operation, these added cations can be expected to migrate slowly toward the cathode (air electrode). The tracer diffusion coefficient of Ca^{2+} in calcia-stabilized zirconia has been measured [42] at temperatures well above the 1000°C operating temperature of the Westinghouse fuel cell. Extrapolation down to 1000°C and use of the Nernst-Einstein relation to convert diffusivity to conductivity suggests that the time it would take Ca^{2+} ions to cross the 20μ electrolyte film under the expected 0.8 volts potential difference might be very long, of the order of hundreds of years. On the other hand, Rhodes and Carter found that the rate of migration of Ca^{2+} ions in grain boundaries is perhaps 1000 times larger at 1800°C than is the bulk diffusion rate, a ratio that would be expected to be even larger at lower temperatures. Hence,

migration of impurity or stabilizing ions along grain boundary paths over significant distances during times of the order of a year or less must be expected in all of the fluorite-structure oxides of current interest as solid electrolytes.

If such a migration away from the anode proceeded to the point where the content of impurity or stabilizing ions changes appreciably, resistive layers would appear at the electrodes or grain boundaries. In the extreme case in ZrO_2 the composition limit at the cubic phase boundaries could be violated and a destabilized layer formed at the anode and a zirconate layer at the cathode. Since oxygen migration is much slower in the non-cubic than in the cubic phases of ZrO_2 , and in the zirconates, the result would be the deposition of essentially non-conducting layers under the electrodes and a deterioration of the cell efficiency.

Even in solid electrolytes other than ZrO_2 , the impurity ions necessary to produce high ionic conductivity must be expected to migrate at least to some extent in the solid electrolyte under the influence of the steady applied field. A number of consequences can result. In particular, the accumulation of such impurities near the electrodes can lead to the development of resistive layers or to interference with the processes whereby electrons are interchanged with oxygen ions by the electrodes. The result would be either an increase in the electrolyte resistivity or in the electrode polarization.

It must be emphasized that these processes are known to occur in stabilized zirconia and are quite likely in other similar oxides. It seems very probable they would result in deterioration. What cannot be predicted on the basis of present knowledge is the rate at which they will occur in the particular solid electrode formulations to be used in fuel cells, and

the extent of property degradation they will produce. However, prudent management would seem to require an effort to explore probable degradation effects as the fuel cell development proceeds, to provide evaluation techniques, and if possible to understand the processes as a basis for developing counter measures.

Research Program

The research program is based upon study of the longevity of fuel cell components for use at high temperature with low BTU gases of the kinds produced by coal gasification processes. In particular, work will be concentrated upon ceria solid electrolytes and processes occurring within the electrolyte and leading to degradation of the electrolyte resistivity, the electrode-electrolyte contact resistance, or the electrode polarization.

The major thrusts of the research will be:

1. Evaluation of real electrolyte-electrode materials with respect to longevity;
2. Development of an understanding of the degradation processes that occur;
3. Development of test methods for the evaluation of candidate fuel cell materials and structures with respect to these degradation processes, with particular emphasis on short-time tests capable of predicting longevity.

In greater detail, the work will be:

1. Evaluation with respect to longevity.

The initial work on the project will consist of a series of experiments aimed at detecting, in as short a time as possible, the operation of degradation processes in real electrode materials.

a. Annealing Procedures

In these experiments, solid electrolyte specimens, both fully electroded and in contact with the appropriate fuel (H_2 plus CO) and air atmospheres, and also provided with sputtered Pt electrodes and in contact with an O_2 atmosphere, will be annealed at a variety of temperatures around the working temperature. For instance, Carter and Roth [39] have found that an ordering reaction in stabilized zirconia occurs, but only below about $1100^{\circ}C$, and the rate depends on temperature. Furthermore, more complex annealing schedules, consisting of nucleation anneals at lower temperatures followed by growth anneals at higher temperatures, may be needed to produce most rapidly the ordering that might otherwise occur slowly. These anneals will be designed to explore how the ordering proceeds, if at all, in real solid electrolyte specimens.

Some of the anneals will be performed with continuous dc electric fields applied across the specimens, in order to examine the potential migration of stabilizing cations and impurity ions. This can be most conveniently done with specimens with symmetrical electrodes (probably sputtered Pt) in a simple air or oxygen atmosphere, with the dc field impressed by an outside source of potential. Increase in temperature and field strength can be used to hasten and therefore render rapidly detectable otherwise extremely slow processes.

Cerium dioxide (CeO_2) doped with trivalent cations [6,7] has been selected as the material for this study. The work will be carried out on hot-pressed specimens of CeO_2 doped with 10 to 30 mole percent yttrium oxide (Y_2O_3) or gadolinium oxide (Gd_2O_3). These specimens will be hot-pressed outside our laboratory to our specifications. In addition, hot-pressed and sintered specimens of materials being used in high temperature fuel cell development projects will be obtained, where possible, from the

appropriate industrial laboratories carrying out the development work. The frequency-dependent conductivities of these specimens will be examined first. They will be characterized further with respect to composition, dopant distribution, microstructure, and mechanical strength.

b. Measurements

Greatest reliance will be placed upon the use of ac complex admittance measurements, during the anneals, to monitor changes taking place in the specimens. The complex admittance can be used, as shown by Bauerle [43], to obtain information about the intrinsic conductivity of the electrolyte, the influence of impurities on the grain boundaries and the rate of electron ion transfer at the electrodes. As Raleigh [44] pointed out, these measurements can be made in the presence of a dc bias and used to explore the limitations of reactant transport to and from the electrodes. We plan to make these measurements during the anneals to monitor the electrochemical properties and to signal changes that arise from degradation processes. These ac admittance measurements will be supplemented by measurements of oxygen transport through the oxide. Electrode polarization will be further studied with cyclic voltammetry. Measurements of electrical properties will be correlated with chemical analyses, SEM studies of microstructure and dopant distribution, and other measurements which may elucidate the defect structure of the electrolytes.

c. Degradation Experiments

Degradation of the ceramic electrolytes will be studied as a function of dopant concentration, oxygen activity, temperature, current density, and time. Two types of studies will be conducted. In the first type of experiment, the current-independent decrease in electrical quality (decrease in ionic conductivity) of the electrolyte will be studied as a function of concentration, temperature, and time. The initial experiments

will be carried out at an oxygen pressure of about 10^{-4} atm. Subsequent experiments may be carried out at both lower and higher oxygen pressures and at values of concentration and temperature as indicated by the previous experiments. For these experiments, specimens will be removed from the annealing furnace at selected times over the course of a 32-week period for the electrical measurements. The second type of experiment will be carried out on specimens in situ to observe the possible migration of dopant cations when the electrolyte is subjected to high current densities.

This study will attempt to show whether degradation of doped ceria electrolytes can be observed within a period of 32 weeks and, if degradation is observed, to describe the degradation and to determine the conditions which influence it.

2. Studies of Degradation Mechanisms

If long-term degradation of the important fuel cell properties is found to occur, the source of the changes will be sought in the mechanisms discussed above. In particular, the development of an ordered structure can in principle be detected by x-ray, electron or neutron diffraction experiments. Special preparation would be required to remove electrodes and prepare the very thin (20 micron) electrolyte layers, and the measurement would only be made when the probable existence of an ordering reaction had been well established by the electrical monitoring.

Impurity and dopant ion migration can be detected and studied by a number of techniques. For the dopant cations, in CeO_2 , the concentration changes should be large enough to be detectable by use of the electron microprobe. In addition, the occurrence of second phases might be detectable by x-ray diffraction and optical and/or electron microscopy. Attempts will

be made to use reversible Pt/O_2 electrodes to probe the dc electrical conductance across the solid electrolyte film to correlate the conductance with observed compositional changes. In particular, transmission electron microscopy should be very valuable in helping to understand the arrangement of grains and ordered domains and their boundaries in the electrolyte. Early detection of changes in this microstructure, including the development and distribution of second phases, will be attempted to correlate with the chemical and electrical measurements.

Where concentrations are small, as in the case of impurity ions, direct detection of migration may not be possible, and resort may be had to indirect experiments on radioactive tracer migration of probable impurities, to correlate with changes observed in the electrical properties.

3. Development of Life Tests

Out of the work proposed above should come an understanding of the basic long-term processes occurring and their impact on the desirable properties. This information will be used to guide an effort to find means to accelerate and characterize these processes, or to find other indicators of their eventual occurrence. The aim is to provide tests that can be run over short times but that may be used reliably to predict the behavior of the electrolyte-electrode systems, and thus to serve quality control and screening functions.

Progress to Date

During this past quarter the initial experiments have been designed, the starting materials have been obtained or ordered, and necessary equipment assembled or ordered.

Ceria (CeO_2) doped with yttria (Y_2O_3) or gadolinia (Gd_2O_3) will be the material studied. Oxide powders of 99.9 and 99.99% purity have been obtained, except for the yttria, for which 99.9% powder has been ordered but not yet

delivered. Arrangements have been made with a near-by commercial laboratory for hot-pressing of specimens from these powders, to achieve high density with uniform grain size.

With the help of Dr. John Mandel, experiments were designed to sample various conditions of composition, temperature, oxygen partial pressure and current density. For each condition at least one replicate experiment will be performed to establish the uncontrolled variation in the experiments. With the exception of oxygen partial pressure, the range of the sampling for each condition will include the probable condition under which a ceramic electrolyte of such material would be used. In addition, we hope that the range is broad enough so that some specimens will degrade within the period of a few weeks. Since it is necessary to keep the number of experiments and specimens manageable, and since the materials appear to be oxygen-ion conductors over wide ranges of oxygen partial pressure, a single oxygen partial pressure, about 10^{-4} atm, will be used for all experiments.

In selecting the experimental conditions, two modes of degradation have been considered. The first is a decrease in oxygen-ion conductivity due to the ordering of the oxygen vacancies or of the dopant cations. "Ordering" experiments will be carried out to measure the change in ionic conductivity with time for various zero-current conditions. Temperature and composition are expected to be the principal conditions which will influence the rate and the extent of ordering of oxygen vacancies or of dopant cations. The second mode of degradation is the development of regions of reduced ionic conductivity due to the build-up or the depletion of dopant cation concentration as a result of the migration of these cations as small secondary currents. "Migration" experiments will be performed to examine the effect of large current densities over long periods on the ionic conductivity of doped ceria.

The two types of degradation experiments can be summarized as follows:

1. Ordering experiments

Specimens: $\text{CeO}_2 + 10, 20 \text{ or } 30 \text{ mol. \% } \text{Y}_{0.5} \text{ or } \text{Gd}_{0.5}$

40 specimens of each composition

Oxygen partial pressure: $\sim 10^{-4} \text{ atm}$

Temperature: 500, 700, 900, 1100°C

Sampling times: 1, 2, 4, 8, 16, and 32 weeks

Procedure: Two specimens of each composition removed from each furnace at the end of each annealing period for electrical measurements; specimens not returned to furnaces after electrical measurements are made.

Expected results: If ordering of the oxygen vacancies occurs, a decrease in the ionic conductivity with increased ordering is expected. Specimens with significant changes in electrical properties will be examined by other techniques.

2. Migration experiments

Specimens: $\text{CeO}_2 + 10 \text{ or } 20 \text{ mol. \% } \text{Y}_{0.5} \text{ or } \text{Gd}_{0.5}$; 6 specimens of each composition

Oxygen partial pressure: dry air

Temperature: Maximum temperature allowed by stability of Pt electrodes, perhaps $\sim 900^\circ\text{C}$.

Current density: $\sim 1 \text{ A/cm}^2$ and 0 A/cm^2 (blank).

Procedure: Periodic electrical measurements will be made on the specimens without removing the specimens from the furnace.

Expected results: Migration of the dopant cation (Y or Gd) as a small secondary ionic current is expected to deplete the dopant cations at the anode and to enhance the concentration at the cathode, thus changing the electrical characteristics of the specimen.

Two furnaces for the 900° and 1100°C anneals of the ordering experiments are under construction. Two transparent furnaces have been ordered for the 500° and 700° anneals of the ordering experiments. A Pt-wound tube furnace is being rebuilt for the migration experiments. The necessary control equipment, etc., is being assembled.

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<p>8. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)</p> <p>This report describes the research plans and initial progress on the NBS program of research on Materials for Fuel Cells. Transition metal carbides, borides, and nitrides ("refractory hard metals", or RHM) are being examined as potential hydrogen oxidation electrocatalysts for use in acid fuel cells. Preliminary screening of 19 carbides and borides has revealed apparent stability in hot (up to 160°C) phosphoric acid for TaB, NbB, NbC, TaC, Mo₂C, and WC. More sophisticated tests for acid stability for these materials are under way. Equipment for examination of the electrochemical behavior of these materials as hydrogen oxidation electrocatalysts in phosphoric acid electrolytes at temperatures up to 150°C is being completed, and tests will be started on these materials shortly. Additional materials in the general RHM class, including a number of nitrides, have been ordered and will be screened for acid stability. More extensive exploration will be made of the properties of TaC and WC as a function of stoichiometry and presence of other metals and oxygen. Plans exist for a parallel study of oxides as oxygen reduction electrocatalysts for acid fuel cells not under support of this project. The current effort is devoted to improving and expanding the facility for electrochemical measurements. The long-term stability of CeO₂-based solid electrolytes, which are promising new candidate materials for the high-temperature fuel cells, is under study. Materials for fabricating specimens of CeO₂ doped with Gd₂O₃ or Y₂O₃ have been obtained or ordered, and arrangements made to hot press them. Experiments have been designed to examine degradation of the</p> <p style="text-align: center;">CONTINUED</p>			
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electrical properties at temperatures from 500°C to 1100°C, with and without a constant current throughout the degradation anneals. Compositions will be chosen around those giving a maximum conductivity, and the oxygen partial pressure will be fixed at a convenient value. AC admittance measurements will be used to monitor the electrical properties. Furnaces and ancillary equipment are being assembled or constructed.

